ORIGINAL PAPER

EVALUATION OF SOME NEW ORGANIC ADDITIVES WITH ALTERNATIVE FUNCTION GROUPS IN CYANIDE-FREE ALKALINE ZINC ELECTROPLATING

ABD EL-SHAFEY I. AHMED[1], ABDELFATTAH F. SHAABAN[2]

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Abstract. *Polymers (I and II) have been prepared based on imidazole and epichlorohydrine. These polymers were used as primary additives in non cyanide alkaline zinc electroplating processes at ambient temperature. At the same time new low molecular weight compounds were used as secondary additives to increase brightening such as pyridinium salts and aromatic aldehyde derivatives. Pyridinium salts were prepared based on pyridine and nicotinic acid while the aldehyde derivatives were based on vertraldhyde and benzaldehyde. The structure of the primary and secondary additives was designed to have different function groups to study the effect of their changing on plating quality such as hydroxyl, carboxylic and sulphonic groups. Concentrations of primary and secondary additives were changed as well as cell current and platting time in order to find the best combination to ensure full brightness. Moreover a try to combine 3 additives with these alternative function groups were performed for a better brightness and uniformity.*

Keywords: *Zinc, polymer, electroplating, brighteners, additives.*

1. INTRODUCTION

Electroplating with zinc can be performed in presence or absence of cyanide compounds. The cyanide method requires a large amount of cyanic compounds which are toxic and have bad effect to environment as the disposal of the operation waste solution is very difficult. At the same time adding chemicals to treat waste solution to remove the residual cyanides complicate the operation process. Thus, from the aspects of operating efficiency, economy, and public safety the use cyanide in zinc plating is not favorable and the tendency to operate cyanide-free plating baths has been increased. The cyanide-free method can be performed in acidic or alkaline baths. The alkaline method has some advantages such as enhancing the corrosion resistance of pure zinc deposits and producing deposits of single-phase alloys with Fe group metals producing excellent protective properties [1]. However, the main problem with them is their poor throwing power and low brightness [2].

Additives are playing an important rule in overcoming these problems. Many organic additives have been used to improve the brightness and uniformity of the deposits [3-5]. The additives can help in increasing the brightening, reducing the grain size and tendency to tree formation, increasing current density range, improving mechanical and physical properties and reducing stress and pitting [5-7]. A number of organic additives are reported in the literature as brighteners. They can be classified into two different types; the carrier (primary

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[1] University of Zagazig, Faculty of Science, Department of Chemistry, Sharkia, Egypt.
E-mails: a.i.ahmed@surrey.ac.uk, aiaibrahiem@zu.edu.eg.
[2] University of Benha, Faculty of Science, Department of Chemistry, Benha, Egypt.

additive or primary brightener) and the brightener (secondary additive or additional brightener). The carrier would enable grain refinement with medium or good brightness while the brightener would have a complementary effect in producing full bright deposits [5].

Water-soluble polyamines [8, 9] or polyamine sulphones [2] were used as organic brighteners in alkaline zinc electroplating, using small amounts of cyanide or without cyanide, examples in Fig. 1. The most common polyamines in use commercially are formed by the reaction of epichlorohydrin with amino containing compounds. The reaction was performed on two steps the first includes polymer preparation while the second is a quaternarization process to the nitrogen atoms present in its structure. It was reported in the literature that tertiary and quaternary amino groups in polyamines is preferred in alkaline cyanide-free zinc baths while primary and secondary amine is preferred in case of alkaline cyanide zinc platting. Using polyamines usually produce smooth semi-bright plate of acceptable commercial quality while in order to produce bright zinc platting, presence of at least one other additive is also required. These other additives could be aromatic aldehydes such as anisaldehyde, veratraldehyde, piperonel, o-, m- and p-hydroxybenzaldehydes, vanillin or pyridinium salts such as 1-benzyl pyridinium 3-carboxylate. The later was reported to be the most preferred secondary additive in cyanide-free zinc plating [8].

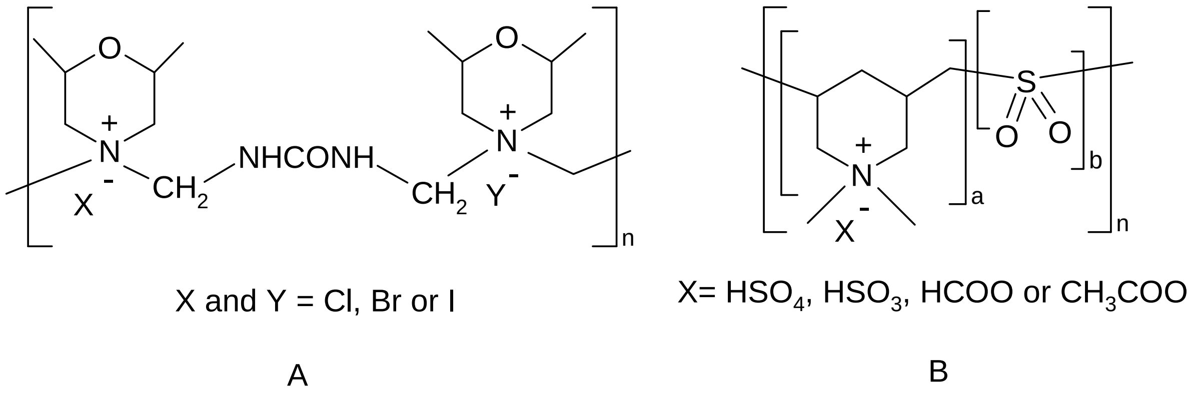


Fig. 1. Examples of polyamines (A) and polyamines sulphones (B).

In this peace of work we are trying to evaluate some polyamines based on imidazole and epichlorhydrine quaternarized using amino or sulphonate containing compounds. This design generates polymeric structures with different structures and high polarity. Moreover some other additives (secondary additives) were applied in addition to the polymeric compounds to help in improving the platting process. The secondary additives were designed to be as modifications to aldehydes and pyridinium salts to increase their polarity. Different combinations between polymers (primary additives) and the secondary additives were evaluated to achieve the best brightening effect. At the same time more than one secondary additive were evaluated in presence of one of the polymers. The additives concentration, cell current and platting time were changed in order to optimize the process at room temperature. The results were compared to plates performed in presence of PVA and vertraldhyde as standard materials evaluate by Shanmugasigamani and Pushpavanam [5] using the same cell to judge the brightening level.

2. MATERIALS AND METHODS

2.1. MATERIALS

Epichlorohydrine, imidazole, Trimethylamine, vertraldhyde, nicotinic acid, allyl bromide and polyvinyl alcohol were obtained from Sigma-Aldrich. Sodium hydroxide, benzyl chloride, zinc oxide, benzaldehyde, sodium hydrogen sulphate and pyridine were applied form El-Nasr Chemicals Co., Egypt. The study was performed using Hull cell 267 ml.

2.2. PRIMARY ADDITIVES

Imidazole (61.3 gram, 0.9 mole) was reacted with epichlorohydrine (83.3 gram, 0.9 mole) in water (200 ml) for 15 hour at 95°C. Another amount of epichlorhydrine (1.8ml) mixed with concentrated HCl (2.4 ml) was added and refluxing was continued for further 6 hours. Trimethylamine (2 ml) in water (5 ml) was added and the refluxing was extended by 5 hours refluxing to form polymer (I). The same procedure was repeated using sodium hydrogen sulphate instead of trimethyamine to form polymer (II), Fig. 2.

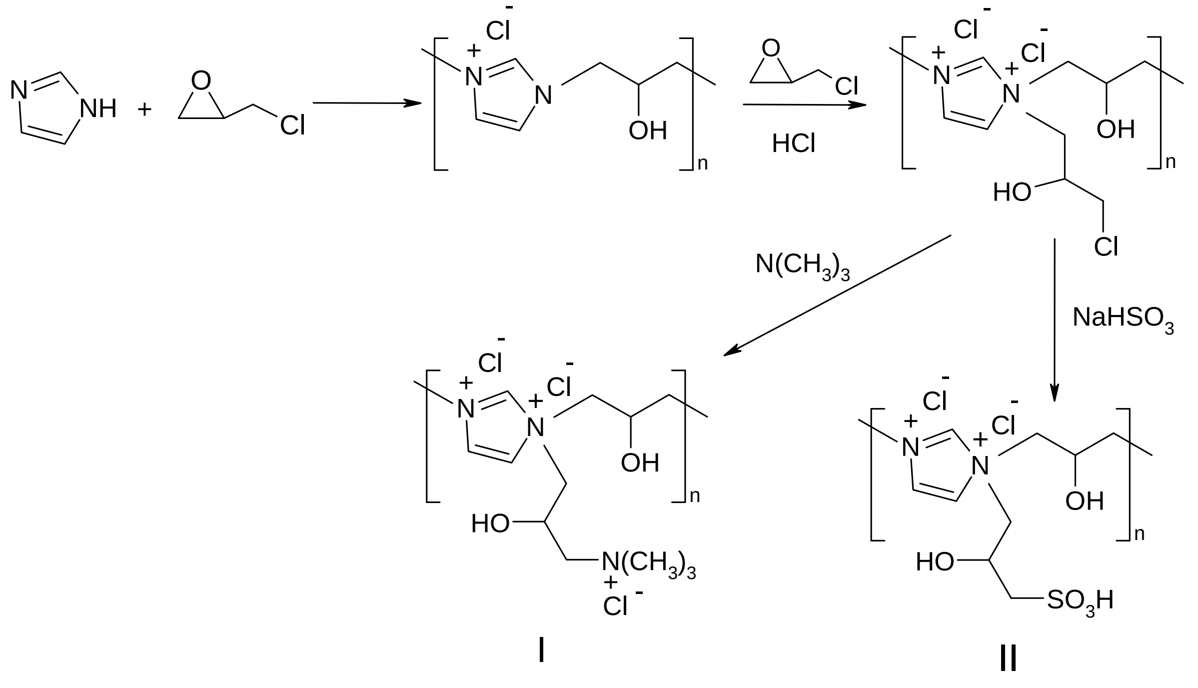


Fig. 2. Preparation of polymers I and II.

2.3. SECONDARY ADDITIVES

Allyl pyridinium bromide was prepared by reacting allyl bromide (1.21 g) with pyridine (0.79 g) at 4°C for 12 hours to form A1 additive, Fig. 3.

Nicotinic acid (6.15 g) was refluxed with benzyl chloride (5.8 ml) in presence of sodium hydroxide (2 g) in water (20ml) for 5 hours to form additive A2, Fig. 3.

Benzaldehyde (10.6 g) was stirred with $NaHSO_3$ (10.4 g) in water (15 ml). A vigorous reaction was happened with formation of white precipitate (A3). The same reaction was repeated using vertraldhyde (16.6 g) instead of benzaldhyde to form A4 additive, Fig. 3.

Pyridine (3.6 ml) was reacted with epichlorhydrine (0.93 g) for 5 hours followed by a reaction with $NaHSO_3$ (1.04g) in water (10 ml) to form A5 additive. The same reaction was performed using nicotinic acid instead of pyridine to form additive A6, Fig. 3.

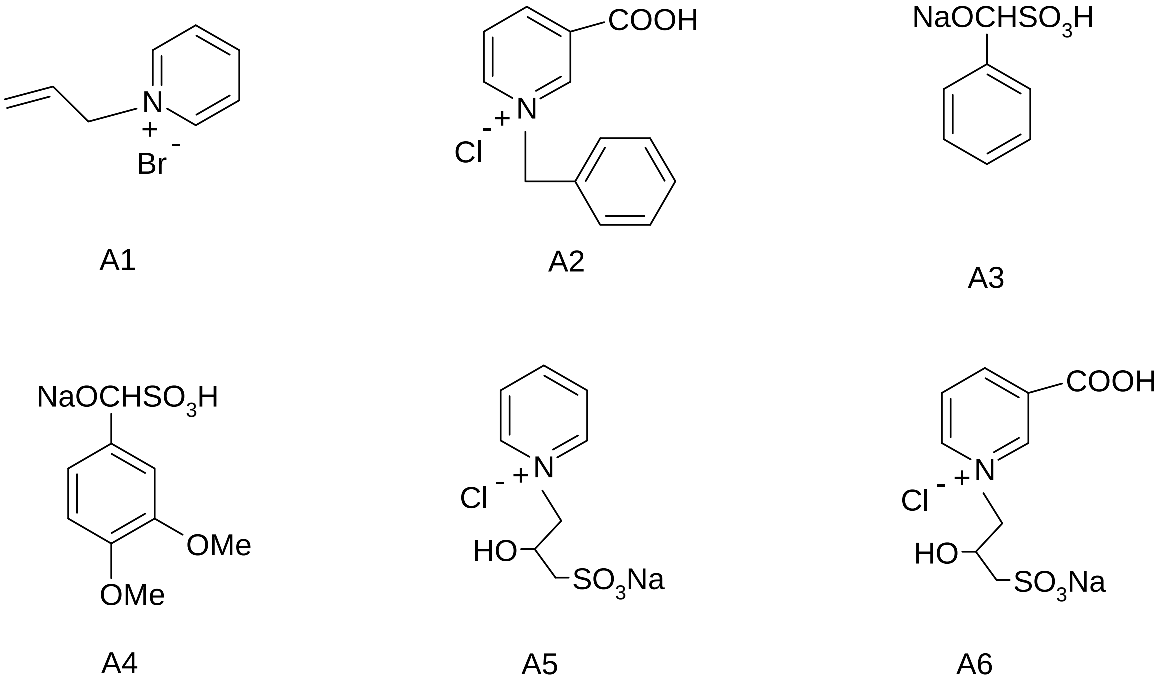


Fig. 3. Examples for the additives that was used in this study.

2.4. BATH CONTENTS (GENERAL METHOD)

Zinc oxide (9 gram) and sodium hydroxide (80 gram) were dissolved in distilled water (1 liter) followed by filtration. Zincate solution (250 milliliter) was transferred to the plating bath which contains zinc electrode while deposition was performed on brass alloy. Twp types of additives were added; primary and secondary while the platting process was performed at different currents and for different time intervals as explained below at the processing section.

2.5. PROCESSING AND OPTIMIZING

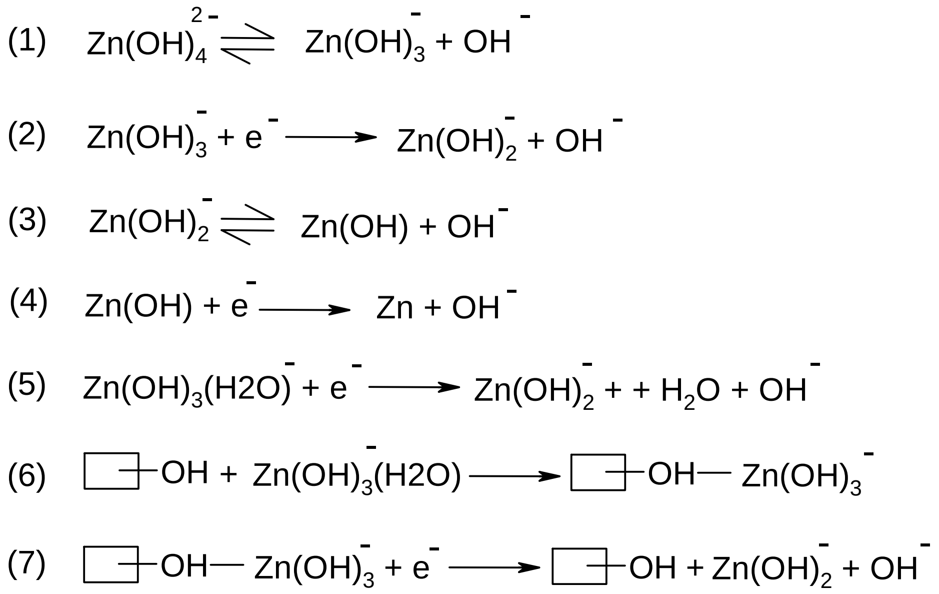
As a start primary additives (polymer I and II) were added to the bath with different ratios; 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.0, 3.4, 3.8 and 4 g/lit while A2 was added with constant concentration of 0.02 g/lit. After selecting the best primary additive its ratio was kept constant while secondary additive was changed from A1 to A6 with constant concentration 0.02 g/lit to select the best secondary additive. As soon as the best secondary additive was identified, its concentration was changed; 0.01, 0.02, 0.03, 0.04 and 0.05 to achieve the best brightening effect. During previous trails the platting was performed at 1 ampere for 10 min at ambient temperature. When all parameters were adjusted to the best (primary and secondary additives) the current of platting process was changed; 0.6, 0.8, 1.0, 1.2 and 1.4 ampere. Moreover the plating time was changed; 1, 4, 6, 8, 10, 12 to 15 minutes with keeping other factors constant. At the same time a ternary system study was performed by adding more than two secondary additives with 1:1 ratio in presence of the primary additive.

For comparison purposes the primary additives (polymer I and II) were replaced with PVA with the same suggested concentrations as above. One of the secondary additives that were suggested by Shanmugasigamani and Pushpavanam such as veratraldehyde [5] was used in combination with PVA to generate samples for comparison purposes under our plating system conditions.

3. RESULTS AND DISCUSSION

Cyanide-free zinc electroplating becomes very important to replace cyanide type due to environmental risks. Organic additives are playing a very important role in producing bright and uniform layers during zinc deposition. One or more additive can be used in the same run. The first was called the carrier or the primary additive and its main job is to help in grain improvement and generate medium brightness. The second was called secondary additive or brightener which used to produce full bright layers of the deposit.

The mode of action of the carrier depends on retarding the rate of ions arrival to deposition sites. Taking PVA as an example, it can be seen from Fig. 4 that PVA is able to retard reaction 5. Zinc deposition involves 4 main reactions, Fig. 4, in which reaction 2 is the rate determining step but zinc ion prefers to exist as a tetra or hexa-coordinate moieties so $Zn(OH)_3^-$ can present as $Zn(OH)_3(H_2O)^-$. In this case equation 2 should be replaced by 5. Reaction 5 is faster than the transporting rate of the ions to the site of discharge. This results in powdery non-adherent deposits formation. In presence of PVA, the rate of equation 5 was retarded and a bright layer is expected due to the low speed of ions moving to the deposition site. PVA could support more hydroxyl ions and due to the polarity of the carbon–oxygen bond, it is possible that it could present with significant amounts in the cathode film, forming a weak physical barrier that hinders the deposition [5]. Moreover, PVA hydroxyls can replace H_2O present in the complex $Zn(OH)_3(H_2O)^-$ holding these ions which retard their movement. In this way reaction (7) will be slower than (5), due to the required energy to break the PVA complex, would explain the grain refining properties of PVA [5]. At the same time the complex form a surface film of polymer around deposition site. To obtain bright zinc from these bath additional organic brighteners (secondary additives) are needed in addition to PVA. These brighteners are smaller molecules having unsaturated and polar sites so they can be attracted to the cathode and influence deposition. These brighteners results as well in breaking the surface film formed by PVA.



(1) $Zn(OH)_4^{2-} \rightleftharpoons Zn(OH)_3^- + OH^-$

(2) $Zn(OH)_3^- + e^- \longrightarrow Zn(OH)_2^- + OH^-$

(3) $Zn(OH)_2^- \rightleftharpoons Zn(OH) + OH^-$

(4) $Zn(OH) + e^- \longrightarrow Zn + OH^-$

(5) $Zn(OH)_3(H2O)^- + e^- \longrightarrow Zn(OH)_2^- + + H_2O + OH^-$

(6) $\square\!-\!OH + Zn(OH)_3^-(H2O) \longrightarrow \square\!-\!OH—Zn(OH)_3^-$

(7) $\square\!-\!OH—Zn(OH)_3^- + e^- \longrightarrow \square\!-\!OH + Zn(OH)_2^- + OH^-$

Fig. 4. The mechanism of PVA action during zinc deposition.

Taking these assumptions in mind polymers (I) and (II) could behave in the same manner due to the presence of hydroxyl groups in their structures which comes from epichlorohydrin and sulphate groups. At the same time these polymers have quaternary nitrogen atoms which may have extra retardation effect on the ions by attracting the complex $Zn(OH)_3(H_2O)^-$. In this study we tried to compare different additives with different function groups in order to reach to the best brighteners with lowest possible costs. So two polymers were prepared to act as primary additive; both of them have quaternary nitrogen atoms in the main polymer chain. At the branch site polymer (I) have extra quaternary nitrogen atom while polymer (II) has sulphonic group.

At the literature the best known secondary additives were aldehydes and pyridinum salts. The structure of these secondary additives was also modified. Aldehydes were modified to incorporate different function groups with high polarity which performed using some simple reactions to produce compounds such as A3 and A4. At the same time some other pyridinum salts have similar features as A2 (which considered a good brightener as mentioned in some researches) were prepared but with different and variety of function groups such as A1, A5 and A6. For example A6 contains carboxylic, hydroxyl and sulphonate groups which increase its polarity and supporting its job as explained above.

The results indicated that platting was achieved with medium quality with increasing the ratio of polymer (I) up to 2.8 g/lit while after this concentration the quality started to decay. Similar results were obtained using polymer (II) but the maximum suitable concentration was 2 g/lit. By changing the secondary additive it was noticed that the best brightness was reported using A2 and A6 using fixed concentration at 0.02 g/lit. For this reason the concentration of both of them was changed in order to reach to the best secondary additive concentration. It was noticed that 0.2 g/lit was the best concentration for A6 while A2 still giving more improvements until 0.4 g/lit. From the previous results it can be seen that the presence of sulphonic group in the primary additives like polymer (II) gives good brightening with lower concentrations than polymer (I) which with quaternary nitrogen atoms in its structure. For secondary additives A2 and A6 achieves the best results. But still the compound with sulphonic groups is showing good results with low concentrations. Increasing the polarity of the function groups increases the polarity of the additive resulting in a better brightening effect. A5 came at the second stage of showing good results followed by A1 while A3 showed the lowest quality. Changing the platting current indicated that the best current to achieve the best brightness was ranging from 0.8-1 ampere while the best time was recorded around 4-6 minutes. The previous results were compared to a plating process generated in presence of PVA as primary additive and veratraldehyde as secondary one; a suggested platting medium in literature [5, 10-12]. It was noticed that plates obtained using polymers (I or II) as primary additives was better than that of PVA under the same conditions which support our assumption that presence of alternative function groups with high polarity could increase the brightening effect.

A ternary system was applied using one primary additive and two secondary ones. The ratio between the two secondary additives was kept as 1:1. All secondary additives (A1-A6) were reevaluated and it was noticed that A2 and A6 still showing the best results using 0.01 g/lit for each of them. This has indicated that presence of A6 beside A2 has succeeded in reducing their required concentration to achieve the same brightening as each one of them separately using 0.02 g/lit for A6 and 0.04 g/lit for A2. Another good result was achieved using mixture between A6 and A4 while the worst one was reported using a mixture between A1 and A3. We believe that this could be explained on the base that A2, A4 and A6 have alternative polar function groups. At the same time the brightening results in presence of this ternary system are better than what was achieved with PVA.

The previous results indicated that applying primary additives in low concentration with different function groups can achieve good brightening effect better than others with hydroxyl groups only. The same phenomena could be seen for secondary additives; a variety of function groups in the compound could support better brightening effect. A ternary system could help in reducing the concentration of used additives and achieving better results. Further efforts will be conducted to generate and evaluate more additives with different function groups in order to increase the possibility of applying them in cyanide-free platting.

4. CONCLUSION

Primary and secondary organic additives were evaluated successfully in cyanide-free zinc platting. Presence of different polar function groups in these additives support its ability to work as brighteners and gives better results that that with hydroxyl groups only. Using ternary systems formed from one primary and two secondary additives with variety of function groups could help in improving the brightening.

REFERENCES

[1] Chandrasekar, M.S., Shanmuga, S., Pushpavanam, M., *Mater. Chem. Phys.*, **124**, 516, 2010.

[2] Zehnder, J.A., Stevens, T.K., *US patent No. 4*, 134, 804, 1979.

[3] Boto, K., *Electrodep. Surf. Treat.*, **3**, 77, 1975.

[4] Pereira, M.S., Barbosa, L.L., Souza, C.A.C., De Moraes, A.C.M.., Carlos, I.A ., *J. Appl. Electrochem.*, **36**, 727, 2006.

[5] Shanmuga, S., Pushpavanam, M., *J. Appl. Electrochem.*, **36**, 315, 2006.

[6] Kavitha, B., Santhosh, P., Renukadevi, M., Kalpana, A., Shakkthivel, P., Vasudevan, T., *Surf. Coat. Tech.*, **201**, 3438, 2006.

[7] Aaboubi, O., Douglade, J., Abenaqui, X., Boumedmed, R., VonHoff, J., *Electrochem. Acta.*, **56**, 7885, 2011.

[8] Rushmere, J.D., *US patent No. 4*, 046, 648, 1977.

[9] Hsieh, J.C., Hu, C.C., Lee, T.C., *Surf. Coat. Tech.*, **203**, 3111, 2009.

[10] Hope, G.A., Brown, G.M., Schweinsberg, D.P., Shimizu, K., Kobayashi, K., *J. Appl. Electrochem.*, **25**, 890, 1995.

[11] Acimovic, S., Lindermann, K.H., Gunz, V.G., *US Patent No. 4166778*, 1979.

[12] Roserberg, W.E., Geduld, H.H., *US Patent No. 3803008*, 1974.